

Characterization of Optical and Associated Properties of Marine Colored Dissolved Organic Material (CDOM)

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LONG-TERM GOALS

A long-term scientific goal of our research for ONR has been to develop an understanding of the physical and chemical processes affecting colored dissolved organic material (CDOM) and the resultant attenuation changes of ultraviolet and visible radiation in seawater, particularly in the coastal environment where complex variations of sources, sinks, and modification processes can result in dynamic and heterogeneous changes to the optical characteristics (attenuation, color) of the surface ocean.

OBJECTIVES

The chemical constituent of seawater that absorbs most of the incident solar radiation is collectively referred to as CDOM. CDOM is a complex aggregate of organic compounds derived from marine biota and terrestrial humic material introduced to the oceans by rivers. The photochemically active fraction initiates most of the photochemical reactions in seawater, altering CDOM itself and affecting the chemical speciation of oxygen, transition metals and various organic compounds. These reactions can have profound effects on the chemical characteristics of seawater and physical properties such as optical absorbance and luminescence. Our primary objective is to understand the differences and similarities between DOM of marine and terrestrial origin, the effects of photochemical processes on the structure and optical characteristics of CDOM and the impact these properties have on the optical characteristics of marine environments.

APPROACH

Our approach to CDOM characterization is to use Flow Field Flow Fractionation (FIFFF) as the separation technique, together with optical characterization of fractionated CDOM by in-line absorbance and fluorescence and structural characterization by LC/MSⁿ. Ion trap mass spectrometry (LC/MSⁿ) is a new and promising technique for the structural characterization of complex refractory organic molecules. To the best of our knowledge this is its first application to marine CDOM. Our principal focus over the last year was to improve methodology for the application of our LC/MSⁿ system to this characterization. Funds from ONR DURIP/1999: “Application of ion trap mass spectrometry (LC/MSⁿ) to the characterization of coastal optical properties (equipment only)” were

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14. ABSTRACT A long-term scientific goal of our research for ONR has been to develop an understanding of the physical and chemical processes affecting colored dissolved organic material (CDOM) and the resultant attenuation changes of ultraviolet and visible radiation in seawater, particularly in the coastal environment where complex variations of sources, sinks, and modification processes can result in dynamic and heterogeneous changes to the optical characteristics (attenuation, color) of the surface ocean.					
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used to purchase additional components. We used a series of riverine and marine DOM samples from South Florida waters as well as purchased terrestrial humic materials for method development and evaluation. We also began photochemical studies using sunlight and UV-laser light sources to determine whether irradiation of fresh CDOM produces material with similar structural and optical characteristics as marine CDOM.

WORK COMPLETED

We completed FIFFF and LC/MSⁿ analysis of samples collected during November 1999 and June 2000 cruises of the R/V Walton Smith, including an extensive series of riverine, coastal and oceanic waters. Two 10-day cruises were accomplished in 2001 (June and September) to examine the differences in optical properties between the wet and dry seasons in south Florida. LC/MSⁿ characterization of samples from the 2001 cruises is underway with results to be presented in the fall

1. Samples:

Samples for FIFFF and HPLC/MSⁿ were collected from river plumes on the southwest coast of Florida, Florida Bay and the Florida Keys reef tract, filtered and stored in the dark for further analytical work in the laboratory. In addition to filtering, samples for LC/MSⁿ were extracted using a new hydrophilic/lipophilic copolymer to increase concentration; improving our ability to see small structural changes in samples through riverine to marine transition zones

2. FIFFF:

Flow Field Flow Fractionation (FIFFF) has been used to characterize colored humic substances by coupling FIFFF to UV absorbance (1-6) and fluorescence detectors (7). The utility of FIFFF techniques for environmental analyses of complex compounds present in low concentrations in natural water has been demonstrated (4). A fifth -year PhD. graduate student, Eliete Zanardi-Lamardo, has been studying CDOM in a fresh to marine transition zone through FIFFF analysis, both in quasi real-time mode shipboard (June 2000) and in the laboratory. A paper about FIFFF methodology for CDOM analysis in natural waters was published recently (7) and continuing efforts are being made to improve the analytical conditions for marine samples with high salinity and low CDOM concentration.

3. LC/MSⁿ:

Results from initial studies combining FIFFF with MSⁿ showed the system could simultaneously determine the fluorescence, UV-Vis. absorption, and mass distribution by both diffusional properties and direct measurement. These results were presented at Pacifichem 2000 (Stabenau, 2000). Certain limitations inherent to ion trap mass spectroscopy caused the mass distributions determined to be narrower than those observed by FIFFF. In order to overcome this limitation CDOM from marine samples need to be concentrated and delivered to the ion trap in a continuous mode while several mass spectra ionization control parameters are scanned. Techniques have been developed to accomplish this, and employed successfully on samples from the June 2001 cruise and are currently being used to analyze samples from the September 2001 cruise. At the start of this year our FIFFF and MSⁿ system relied on a single HPLC system, limiting research productivity and presenting the potential harmful interaction of organic solvents, necessary for LC/MSⁿ operation, with the FIFFF membrane. Purchase of a new HPLC system with fluorescence detector has allowed the simultaneous operation of the

LC/MSⁿ system and FIFFF systems for methods development and eliminated the chance of harmful solvent interactions.

RESULTS

A series of natural water samples from Shark River (SR) in southwest Florida and from its river plume in Florida Bay was analyzed. Absorbance, fluorescence and TOC were correlated with salinity increase, indicating mixing (dilution) of the fresh river water containing high levels of DOM with low-DOM bay waters. However, the optical properties (absorbance at 300nm; fluorescence Ex:350, Em: 495) had different slopes than TOC, suggesting photochemical and biological degradation processes operate simultaneously with the mixing processes and are also significant.

The fractograms for a series of samples in the Shark River plume (Everglades National Park, Florida) show similar molecular mass distributions, which decrease in abundance from the fresh river water to marine samples in the coastal region (Figure 1). Diffusion coefficient (D) and molecular mass distributions (MM) were calculated for the samples. D varied from 3.81 to $4.35 \times 10^{10} \text{ m}^2 \text{ s}^{-1}$ which is in the range of values previously published for humic and fulvic acids (1,6). Two different MM fractions (2 peaks), based on the maximum peak intensities, were found in low salinity water samples based on their fluorescence. Most of the material was in a fraction centered at ~2 kDa and the freshest samples also had a small peak for a larger fraction, ~13 kDa. An interesting feature is that the fluorophores were centered at lower molecular mass distribution than chromophores, suggesting that some absorbing moieties either do not fluoresce or fluoresce less intensively. The peak maximum for the absorbance fractograms shifted downward with increasing salinity, but the same behavior is not observed in the fluorescence measurements

Irradiating a river sample with sunlight produced a fractogram characteristic of marine waters with similar decrease in optical properties, no shift in MM distribution of fluorophores and a 10% shift to lower MM chromophores, as observed in natural samples. These results suggest that photochemical processes are an important mechanism in altering the molecular and optical characteristics of CDOM in surface waters during the flow of the source toward to the sea.

Initial analysis of Shark River CDOM by combined FIFFF-MSⁿ indicates some mass specific removal processes, and not just simple dilution, are occurring (Figure 2). Experiments are underway to determine the relative degree photochemistry and dilution play in these processes. Figure 3 also shows an average mass distribution that is lower than that observed by FIFFF. We have determined that this is a system artifact and developed a technique to overcome this limitation and produce a more representative mass distribution. Using this new technique, samples from the Shark River show average mass of approximately 1.3 kDa with masses observed up to 2.2 kDa, in good agreement with that determined by diffusional properties in FIFFF.

Combined, work to date has shown the power and flexibility of the FIFFF-MSⁿ system to operate in several modes. Specifically it can be used for the:

- determination of average mass during inline analysis of FIFFF effluent
- determination of full mass distribution during direct continuous infusion of concentrated CDOM
- analysis of repetitive structural features during automated MS².

- observation of structural changes induced by controlled photochemical experiments or natural processing.

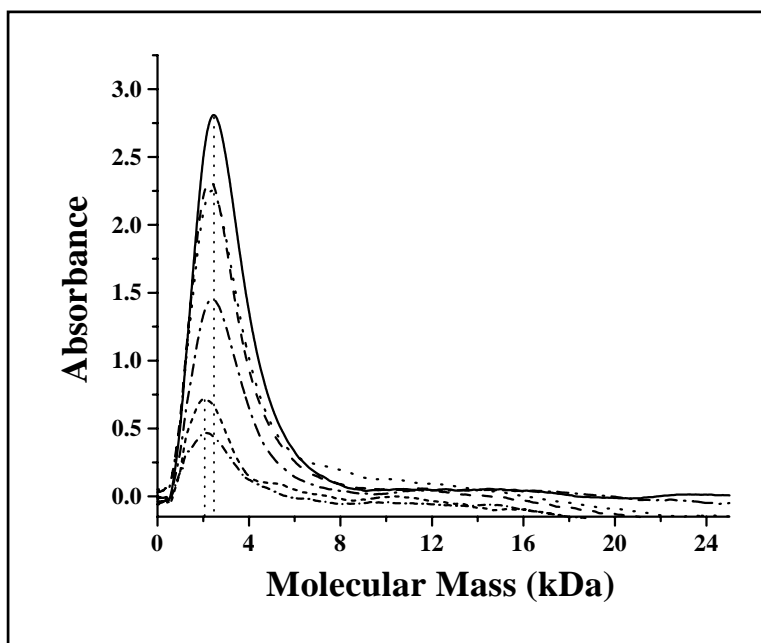


Figure 1: Absorbance (330nm) as a function of molecular mass (kDa) for a fresh to more marine transition zone in the SR. Some representative stations are shown: Salinity: 20.1 (---); 22.1 (--); 22.3 (•••); 24.0 (- • - • -); 28.6 (---); 30.1 (-••-).

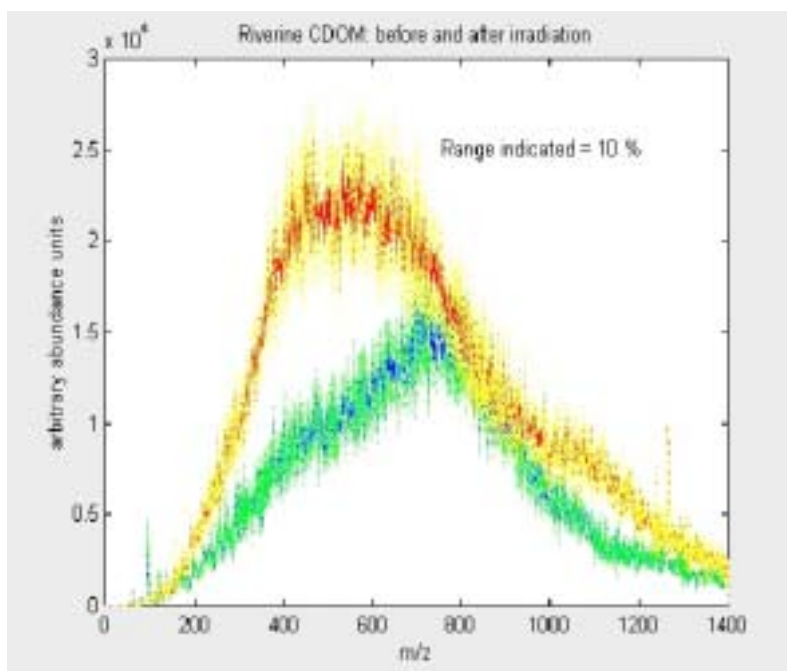


Figure 2: Mass distribution comparison of photodegraded Shark River CDOM (lower) with non-irradiated sample (upper). Decrease in abundance was observed in masses both above and below the 750 to 900 m/z range possibly indicating more photolabile compounds in these ranges.

Two papers on ONR funded research have been presented at Pacificchem 2000 meeting by the graduate students who are responsible for this work. Additionally, the P.I. for this project presented our results at the 2000 ASLO conference.

IMPACT/APPLICATIONS

The means by which we have studied CDOM is novel and appropriate for future investigations of the structural and associated optical features of this material. Our results suggest that the photochemical degradation of terrestrial DOM from rivers forms a significant fraction of marine CDOM in coastal zones. This has significant impacts for the cycling and sources of DOM in the ocean. Correlating changes in optical characteristics with associated changes in structural features under the action of sunlight will allow us to understand how changes in ultraviolet/visible radiation occur in seawater and coastal environments. Aside from developing an understanding of the factors affecting the chemistry and physics of light in the ocean, there are other more applied potential future impacts in the development of new analytical system approaches for examining complex organic substances in the environment.

TRANSITIONS

Our results suggest that FIFFF is a powerful technique to understand the distribution size and optical properties of CDOM in fresh and marine waters. It is a promising tool to elucidate the behavior of complex CDOM molecules and associated photoprocesses in the environment. Coupling FIFFF as the separation technique with structural characterization by LC/MSⁿ is a promising route to elucidating the behavior of CDOM and potentially other complex organic substances in marine systems. For example, the LC/MSⁿ system has been used in a study of marine coral proteins by members of the Marine Biology and Fisheries Division at RSMAS. In general, we see a strong future for the transition of the FIFFF and LC/MSⁿ instrumentation/ techniques to the study of other complex organic systems (eg. volatile organic carbons and polyaromatic hydrocarbons in aerosols), both in this laboratory and elsewhere.

RELATED PROJECTS

Work on developing an autonomous oceanographic monitoring system for vessels of opportunity, including superyachts and commercial cruise liners, has led to cooperation with SeaPoint Sensors, Inc. (Rhode Island) to develop a solid state CDOM sensor. A program of deployment and comparison to traditional on-line fluorometers was partially funded by ONR.

REFERENCES

- (1) Beckett, R.; Jue, Z.; Giddings, J.C., *Environ. Sci. Technol.*, **1987**, 21: 289.
- (2) Beckett, R.; Bigelow, J.C.; Jue, Z.; Giddings, J.C.; In: *Aquatic Humic Substances*, Suffet, I.H.; MacCarthy, P., Eds., American Chemical Society, Washington DC, **1989**, p.68.
- (3) Hasselov, M.; Lyven, B.; Haraldsson, C.; Sirinawin, W., *Anal. Chem.*, **1999**, 71: 3497.
- (4) Lyven, B.; Hasselov, M.; Haraldsson, C.; Turner, D.R., *Anal. Chim. Acta*, **1997**, 357: 187.

- (5) Thang, N.M.; Geckeis, H.; Kim, J.I. and Beck, H.P. *Colloids and Surfaces*, **2001**, 48: 289.
- (6) Lead, J.R.; Wilkinson, K.J.; Balnois, E.; Cutak, B.J.; Larive, C.K.; Assemi, S.; Beckett, R., *Environ. Sci. Technol.*, **2000**, 34: 3508.
- (7) Zanardi-Lamardo, E.; Clark, C.D.; Zika, R.G., *Anal. Chim. Acta*, **2001**, 443: 171.

PUBLICATIONS

Zanardi-Lamardo, E., Clark, C.D. and Zika, R.G. (2001), “Frit Inlet/Frit Outlet Flow Field Flow Fractionation (FIFFF): Methodology for Colored Dissolved Organic Material (CDOM) in Natural Waters”, *Anal. Chem. Acta*, **443(2)**: 171-181.

Clark, C.D., J. Jiminez, E. Zanardi-Lamardo, R. Zika and G. Jones II (2001), “Fluorescence Lifetimes of Dissolved Organic Matter in a Riverine to Marine Transition Zone”, *Mar. Chem.* In press.

Zanardi-Lamardo, E., Clark, C.D., Moore, C.A. and Zika, R.G. 2001. Determination of the Molecular Mass and Optical Properties of Colored Dissolved Organic Material (CDOM) in River and Coastal Waters by Flow Field-Flow Fractionation (FIFFF). Submitted to *E.S.T.*

PRESENTATIONS

Stabenau, E.; E. Zanardi-Lamardo, E.; C.D. Clark and R.G. Zika. “Optical Characterization of a Transect from Caloosahatchee River to Gulf of Mexico”, oral presentation, Pacificchem, 2000.

Zanardi-Lamardo, E.; E. Stabenau; C.D. Clark and R.G. Zika. “Photochemical Studies and Characterization of Coastal Waters in Southwest Florida”, oral and poster presentation, Pacificchem, 2000.